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Studies In Vapor Pressure

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Studies In Vapor Pressure

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The author desires to express his appreciation to Professor A. W. C. Menzies at whose suggestion and under whose direction the work herein described was carried out.

THE RATE OF ATTAINMENT OF VAPOR PRESSURE EQUILIBRIUM IN LIQUIDS

BY WILLIAM A. WEST

In his presidential address to the London Chemical Society in 1927, H. B. Baker[1] reported that the vapor pressures, measured at room temperature, of certain undried liquids were appreciably raised by previous prolonged treatment at high temperatures. He considered that this was due to a delay in attainment of internal equilibrium. This would be similar to the well-known results of heat treatment of metals. It seemed to be desirable to investigate this phenomenon more fully, since, if it were so, vapor pressure of a liquid would be a function of time of heating, previous treatment of material, etc. Consistent vapor pressure measurements could then be obtained only by following a standardized procedure, based on observations of the rate of attainment of equilibrium in the liquid in question.

A. *Method.*

We used two isoteniscopes,[2] which were dried, filled with samples of the same liquid, and then boiled out in a bath near room temperature till they showed identical pressures. One was then closed, either by sealing off or with a mercury seal, and heated for some time in an oven or a glycerine bath. It was then brought back to the original bath, opened, and the vapor pressure compared with that of the unheated one. (In the case of liquid sulfur a different procedure was employed, as described later).

The sensitivity of the method was from 7 to 15 times that of one employing a mercury column for pressure measurements, according to the density of the liquid used. Baker made use of the classical barometer tube method.

B. *Liquids Investigated.*

1. Normal behavior expected.

Benzene, purified and dried over sodium. This is generally considered to be a normal liquid, except perhaps when intensively desiccated.[3]

Water. Although this is believed to have an internal equilibrium between different molecular forms, this equilibrium is attained practically instantaneously. Baker obtained a negative result by his method.

2. Abnormal behavior possible.

Acetone.

Ethyl alcohol, absolute.

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[1] J. Chem. Soc., **1927**, 951.

[2] Smith and Menzies: J. Am. Chem. Soc., **41**, 1419 (1910).

[3] Baker: J. Chem. Soc., **1922**, 570.

Acetic acid, M.P. 16.6°, B.P. 117.8°. The material had been subjected to fractional crystallization till the melting point became constant within 0.02°, and was then distilled twice within a range of 0.02°.

These three, having respectively carbonyl, hydroxyl, and carboxyl groups, might be expected to show molecular association, and therefore an internal equilibrium which might not be very rapidly attained. Acetic acid undoubtedly does have such an internal equilibrium, and it was reported by Baker to show a marked lag in attainment of vapor pressure equilibrium.

3. Abnormal behavior probable.

Liquid sulfur. The evidence for the existence of an internal equilibrium is well-known. Also, the extremely high viscosity[1] over the temperature range 160°–250° would seem to favor a retardation of equilibrium attainment.

In all cases where the material was distilled at least a week was allowed to pass before using it, to permit equilibrium at the lower temperature to become established.

C. *Results.*

1. Tabulation of results for the first five liquids.

	1	2	3	4	5	6	7
Benzene	18	120	25	6	0	sealed	oven
Water	6	119	35	10	−1	"	"
Acetone	23	120	25	5	0	"	"
Alcohol	19	113	20	8	0	Hg seal	Glycerine bath
Acetic acid	18	145	20	4	0	" "	" "
Acetic acid	20	140	20	5	0	" "	" "

Column 1: time of heating. (hours).
2: temperature to which heated. (°C)
3: temperature of comparison bath. (°C)
4: time between removal from heating and first reading (min.)
5: increase in v. p. of heated isoteniscope. (in mm of liquid used)
6: method of closing isoteniscope.
7: method of heating.

No increase in vapor pressure was observed. In the case of water the slight lowering is thought to be due to its having dissolved material from the glass.

2. Liquid sulfur.

After boiling out at a higher temperature the isoteniscopes were brought to 215°, a nitrate bath being used. One was then raised into a glass cylinder kept at 150°. It is well known that the dark red, viscous form of sulfur becomes pale yellow and mobile when cooled below about 160°. After giving ample time for this change to take place, the isoteniscope was lowered

[1] Farr and McLeod: Proc. Roy. Soc., 97, 80 (1920).

again into the bath, and compared with the one which had remained there. Thus the sulfur would change to the viscous form, rise in temperature through the range of greatest viscosity, and finally come to equilibrium where the viscosity was not much below the maximum.

A mixture of sodium and potassium thiocyanates was used as a confining liquid in the isoteniscope. This was liquid at 140°, and provided a non-objectionable, mobile, confining fluid.

Two observations were made:

Temp. of bath	215
Temp. of cylinder	150
Time in cylinder	45 min.

In each case, the vapor pressure of the previously cooled isoteniscope rose slowly, till, in about 4 min., it became equal to that of the comparison instrument. It is considered that this shows no delay in attainment of vapor pressure equilibrium at all distinguishable from the ordinary lag in thermal equilibrium.

D. *Explanation of Baker's Result for Acetic Acid.*

During this investigation, work in this laboratory by Dr. Sydney L. Wright (to be published), showed that the acetic acid used by us could be divided into fractions whose vapor pressures differed by as much as 4 mm of mercury at the boiling point, by very slow isothermal distillation in a special form of apparatus. This was undoubtedly due to its water content, in spite of its having been twice distilled within a range of 0.02°. Since Baker mentions no special precautions in purifying his material, we feel justified in assuming that it was not superior to ours.

When Baker's barometer tube containing acetic acid above the mercury was placed in the heated bath, the vapor at equilibrium with the liquid would contain a larger proportion of the more volatile constituent. When cooled, this vapor would largely condense, forming a more volatile layer on the surface of the meniscus, and therefore increasing the observed vapor pressure. On standing, diffusion in the liquid would eventually bring the vapor pressure back to normal.

An instrument was designed to test this explanation. (see cut). The bulb C was filled with acetic acid and thoroughly boiled out, being held in an inclined position. Stopcock G was then closed and the instrument brought back to the vertical, so that the liquid was all driven into bulbs B and E and the connecting tubes, the only vapor being in bulb C. The right-hand part of the apparatus was placed in a bath at 20°, the column of liquid was adjusted to a marked point A by changing the quantity of mercury in bulb E, and the reading of the mercury manometer D taken. After heating in a glycerine bath at 80° for 18 hours, the instrument was brought back to the bath at 20°, care being taken not to permit large or sudden movements of the meniscus during cooling. The manometer was read again, then the liquid from bulb B was allowed to rise into C, gently agitated, drawn down again

to A, and the manometer read a third time. This was done with the acetic acid previously used, and also with another sample of melting point 16.5°.

M.P. of acid	Change in pressure after heating 18 hr.	After mixing
16.5°	+4.0 mm Hg	Increase disappeared and v.p. returned to original value.
16.6°	+0.6 " "	

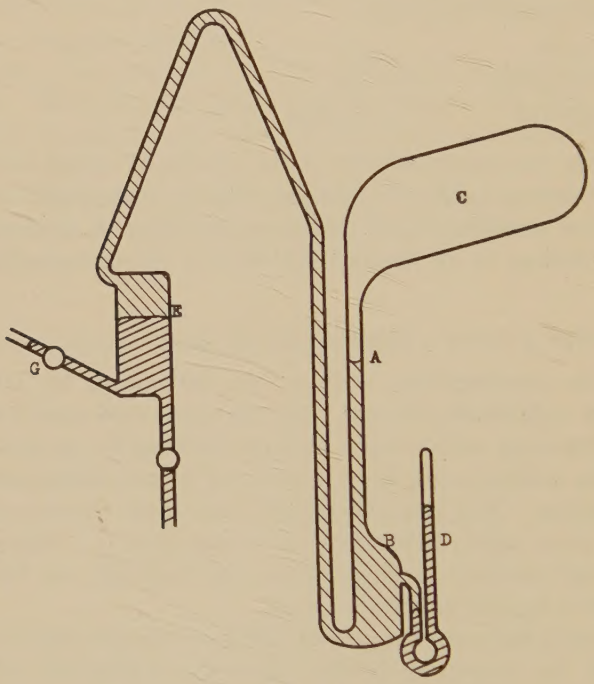

FIG. 1

Baker heated his material 24 hours at 80°, and found an increase in vapor pressure of 2 mm, which had disappeared one week later. There is of course no reason to expect quantitative agreement between our results and Baker's but the magnitude of the effect found appears to be about the same.

Summary

1. Six liquids, of different types, have been tested for delay in attainment of vapor pressure equilibrium with change in temperature. In five cases the comparison temperature was similar to that used by Baker.

2. The temperature of heating varied from 65° to 125° above the comparison temperature, and the limit of observable pressure difference averaged less than 0.05 mm of mercury.

3. In no case was a delay in vapor pressure equilibrium found which was distinguishable from the lag in thermal equilibrium.

4. An explanation is offered, supported by experimental evidence, for the result obtained by Baker for acetic acid.

THE VAPOR PRESSURES OF SULFUR BETWEEN 100° AND 550° WITH RELATED THERMAL DATA

BY WILLIAM A. WEST

No previous observer of the vapor pressures of sulfur has extended his measurements over a range of more than 200°, and only in two cases, (below 120° and from 390° to 445°), do the results of different observers overlap by more than one or two readings. In every case, marked divergence is found between the values of different observers, (see later tables), so that reliable knowledge of either the absolute value of the vapor pressure or of the shape of the curve, over any extended range, has been impossible. The only exception is the neighborhood of the boiling point, where much work has been done, which has been summarized by Mueller and Burgess,[1] with the adoption of 444.60° as the accepted value of the sulfur boiling point.

In an attempt to clear up this unsatisfactory situation, a series of measurements has been made extending from 104° to 543°, over a pressure range of 250,000-fold. An equation has been computed which appears adequately to represent the vapor pressure curve over this range. From this equation the related thermal data have been calculated.

I. Experimental Methods

A. *Thermometry.*

Temperatures were measured by means of a platinum resistance thermometer, of the compensating lead type, wound on mica, with a "Vitreosil" opaque-silica protecting tube. It was calibrated against the freezing and boiling points of water, and the melting point of zinc. The first two were determined in the usual way, and the last by using Melting Point Zinc, No. 43b, as supplied by the Bureau of Standards, the given melting point being 419.43°. Difficulty was at first experienced in obtaining consistent results with the ice point, due to soluble material persistently remaining in the pores of the silica tube. It was found that this could be remedied by steaming out in the boiling flask for one hour, after which constant and consistent results were always obtained. A tube of transparent quartz would have obviated this difficulty.

Resistances were measured by means of a Mueller Type Thermometer Bridge, made by Leeds and Northrup. The makers supplied calibration data showing no deviations which would affect our results. We checked the various resistances of the bridge against each other, and found no discrepancies worth taking into account. For temperatures above the range of the

[1] Scientific Paper, Bureau of Standards, No. 339 (1919).

bridge, (260°, for our thermometer), a supplementary resistance was used, whose value was determined before and after each series of observations.

An e.m.f. of 2 volts was used in the bridge circuit, which gave an amperage through the thermometer well below that at which objectionable heating might occur.[1] The galvanometer was of such sensitivity that a change of resistance corresponding to 0.002° gave a perceptible deflection. The thermometer head was enclosed in a wooden box, and no thermal e.m.f. amounting to as much as 0.01° in the measurement was observed, although a reversing switch was used throughout.

The fixed points, and the constants of the Callendar formula, which were determined every two weeks, showed the usual slow progressive change, (see Mueller and Burgess: loc. cit.), but this was very small in amount. The following values were obtained at the beginning and end of the work:

	Jan. 7	Mar. 12
F.P. water	25.990 ohm	25.983 ohm
B.P. water	35.996 "	35.987 "
F.P. zinc	65.929 "	65.926 "
F.I.	10.006 "	10.004 "
δ	1.511	1.505

As already stated, the accepted value of the S.B.P. is 444.60°. Four observations were made near the boiling point, and were reduced to 760 mm by the Mueller and Burgess formula.[2] The value obtained was 444.57° ± .01, which agreement gives confidence in the calibration of the thermometric instruments.

B. *Vapor Pressure Measurement*

1. By the static isoteniscope method. This instrument and its use have been described by Smith and Menzies.[3] It was used for all pressures above 6 mm, and for a few below. From 20 to 1200 mm the pressures were measured by a closed mercury gauge, exhausted to below 0.01 mm. For pressures above 1200 mm the gauge was open to the air, the barometric pressure being given by a barometer previously corrected by comparison with the gauge readings. The arrangement of the apparatus and the determinations of corrections were similar to those described by Smith and Menzies (loc. cit.), except that a steel bar was used for the gauge scale, instead of a tape.

Pressures below 20 mm were measured by a McLeod gauge, the following procedure being used. The pressure was adjusted to the desired value, and then the temperature of the bath was changed a few hundredths of a degree at a time, till the liquid in the limbs of the isoteniscope became level, and remained so for at least 5 min. The viscosity of sulfur at this temperature, (210°–250°), is such that even this procedure cannot give results of

[1] Mueller and Burgess: Bull. Bur. of Standards, 6, No. 2.

[2] Scientific paper, Bureau of Standards, No. 339 (1919).

[3] J. Am. Chem. Soc., 32, 1419 (1910).

high precision, at least at the lower end of the range. Nevertheless, measurements were made, to serve as an approxinate check on the method next described.

2. By the vaporization bulb method. This method has been previously used by Menzies.[1] The form of apparatus finally adopted for use with sulfur is shown in Fig. 1. The 250 cc bulb A contained several grams of sulfur. It was repeatedly boiled out, and pure, dry nitrogen was admitted and pumped out to remove foreign gases. The measurement was then made as described by Menzies.

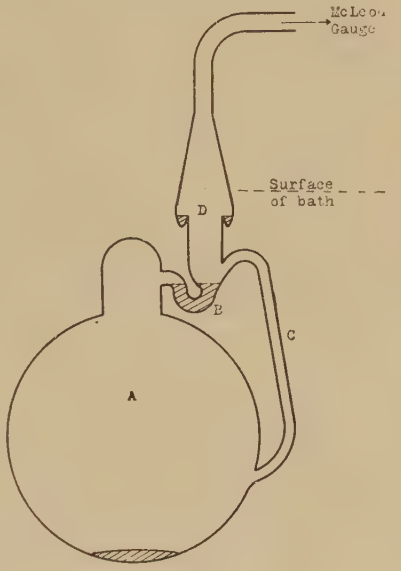

FIG. 1

This method is based on the following assumptions:

i. That the inert gas is not appreciably soluble in liquid sulfur. This was tested for by using different quantities of sulfur and pressures of nitrogen, and no indication of measurable solubility was found.

ii. That the bulb is filled with sulfur at saturation pressure. Preliminary experiments with a straight tube instead of the trap B, showed this not to be the case. A falling off at higher pressures was always observed. This appeared to be due to inability of the sulfur in the bottom of the bulb to maintain saturation pressure, while rapid diffusion was going on to the condensing surface in the tube. This effect is especially marked in the case of sulfur, since the high viscosity prevents running back of the liquid, down the tube and the sides of the bulb. The trap, and the small-bore connecting tube C, overcame this difficulty, since the extreme slowness of diffusion through tube C insured complete saturation in the bulb.

iii. That the pressure is the same throughout the system. A slight falling off at high vapor pressures was still observed (not more than 0.1 mm). This was thought to be due to back pressure caused by the rapid movement of sulfur vapor in the tube, from above the trap to the condensing surface. This would result in a relative lowering of pressure in the gauge part of the system. To remedy this the enlargement D was introduced, with an annular depression to hold sulfur. This was intended to reduce to a minimum the movement of sulfur vapor, by providing a source quite close to the condensing surface.

The guarantee that the sources of error have been overcome, is the agreement of the highest pressures so measured with the mean of those observed by the isoteniscope at the same temperatures. At lower vapor pressures the

[1] J. Am. Chem. Soc., **42**, 2218 (1920).

effects would, in any case, be much less. Also, overlapping ranges of pressures, measured with different pressures of nitrogen, were found in substantial agreement. (See later tables.)

Three McLeod gauges, of different capacities, were used, in order to obtain the maximum sensitivity for each range of pressures.

C. *Temperature Regulation.*

For the vaporization bulb method, an oil bath of 4 liter capacity was used; for the isoteniscope, a nitrate bath,[1] the container being a 2 liter beaker in an asbestos jacket, covered with a double thickness of asbestos board. Violent stirring was provided in each case. The temperature was regulated by adjusting one or more gas burners; with the nitrate bath, control was possible to within 0.01°, but with the oil bath the uncertainty was somewhat higher, though still well within the accuracy of pressure measurements. Lack of uniformity of bath temperature was tested for by making observations with the thermometer at different depths, and identical results were obtained. It may be noted that above 500° the nitrate bath quite appreciably attacks Pyrex.

D. *Purity of Material.*

Commerical roll sulfur was purified by fractional distillation followed by four complete distillations, in vacuo for one sample, in nitrogen at atmospheric pressure for another. It is well known that black spots continue to appear in sulfur, even after several distillations. This discoloration was observable in the material distilled in vacuo, but almost entirely absent in that done in nitrogen, perhaps because the higher temperature more completely and rapidly decomposed the organic matter responsible. Both samples gave identical vapor pressure results.

Mueller and Burgess (loc. cit.) have found that commercial sulfur gives a boiling point almost identical with that of the purified material. We tested this by the static method with the following result.

Isoteniscope filled with commercial roll sulfur. Boiling points (reduced to 760 mm) are given.

1.	After brief boiling out	444.44
2.	" " " "	444.47
3.	" " " "	444.51
4.	" thorough " "	444.56
5.	" " " "	444.57
6.	" standing 10 min.	444.44
7.	" thorough boiling out	444.56

When freshly boiled out, roll sulfur yields a value identical with that for purified sulfur, but on standing, volatile matter seems to appear, which slightly lowers the observed boiling point. Nothing of this sort was observed with the purified sulfur. The effect may be due to the decomposition of the

[1] Menzies and Dutt: J. Am. Chem. Soc., 33, 1366 (1911).

organic matter present, or to the formation of a small amount of CS_2. This slow liberation of volatile matter would, of course, be entirely negligible in its effect on the dynamically determined boiling point.

II. Results

A. *Our own results.*

Our results are tabulated in the first two columns of Table I. In the column headed Method, "B" indicates vaporization bulb, the number following designating the series: "B1" with the most sensitive McLeod gauge,

TABLE I

Our Results (mm of mercury)

No.	Temp. °C	p. obs.	p. calc.	diff.	percent	method
1	103.48	0.011	0.0092	+.0018	+19.5	B_1
2	115.88	0.026	0.0228	+.0032	+14.0	B_2
3	117.03	0.023	0.0247	−.0017	− 6.9	B_1
4	123.30	0.040	0.0378	+.0022	+ 5.8	B_1
5	134.44	0.076	0.0776	−.0016	− 2.1	B_2
6	152.30	0.218	0.220	−.002	− 0.9	B_2
7	156.16	0.28	0.271	+.009	+ 3.3	B_3
8	172.90	0.630	0.636	−.006	− 0.9	B_2
9	175.68	0.72	0.724	−.004	− 0.6	B_3
10	196.90	1.94	1.86	+.02	+ 1.1	B_3
11	213.20	3.72	3.57	+.15	+ 4.2	Is_1
12	214.20	3.83	3.71	+.12	+ 3.2	Is_1
13	219.94	4.56	4.60	−.04	− 0.9	B_3
14	223.74	5.20	5.27	−.07	− 1.3	Is_1
15	227.45	6.30	6.01	+.29	+ 4.8	Is_1
16	227.59	5.94	6.04	−.10	− 1.7	B_3
17	246.84	11.80	11.48	+.32	+ 2.8	Is_1
18	251.37	13.02	13.22	−.20	− 1.5	Is_1
19	271.12	23.80	23.65	+.15	+ 0.6	Is(5)
20	298.64	48.7	48.79	−.09	− 0.2	Is
21	328.54	97.40	97.71	−.31	− 0.3	Is(7)
22	364.40	202.1	201.6	+.5	+ 0.2	Is(2)
23	387.55	307.5	306.8	+.7	+ 0.2	Is
24	413.09	470.5	470.2	+.3	+ 0.1	Is
25	444.57	760.0	760.0	—	—	Is(4)
26	467.33	1045.2	1047.2	−2.0	− 0.2	Is
27	478.78	1225.8	1228.3	−2.5	− 0.2	Is
28	483.01	1286.6	1293.5	−6.9	− 0.5	Is
29	487.23	1354.7	1363.9	−9.2	− 0.7	Is
30	490.73	1416.0	1422.6	−6.6	− 0.4	Is
31	503.95	1675.3	1680.2	−4.9	− 0.3	Is
32	543.08	2689.2	2675.2	+14.0	+ 0.5	Is

nitrogen pressure at room temperature 0.184 mm; "B_2," the intermediate gauge, nitrogen pressure 0.378 mm; "B_3" the least sensitive gauge, nitrogen pressure 1.96 mm. "Is" indicates isoteniscope and mercury gauge; "Is_1," isoteniscope and McLeod gauge. The numbers following Nos. 19, 21, 22, and 25, indicate that the result given is the mean of such number of observations, taken very close together. No. 25 is reduced to 760 mm by the Mueller and Burgess formula.

TABLE II

Vapor Pressures of Sulfur calculated from Our Equation

Temp. °C	p (mm Hg)	Temp. °C	p (mm Hg)	Temp. °C	p (mm Hg
120	0.030_4	270	22.9	420	524.4
130	0.058_7	280	30.2	430	612.1
140	0.10_9	290	39.3	440	710.7
150	0.19_4	300	50.4	450	822.1
160	0.33_2	310	64.1	460	946.5
170	0.55_2	320	80.7	470	108_6
180	0.88_8	330	100.6	480	124_1
190	1.39	340	124.3	490	141_4
200	2.1_2	350	152.5	500	160_5
210	3.1_6	360	185.4	510	181_5
220	4.6_0	370	223.9	520	204_8
230	6.5_6	380	268.5	530	230_3
240	9.1_9	390	320.2	540	258_3
250	12.7	400	379.5	550	287_0
260	17.2	410	447.2		

It was found impossible to represent these observations by a 3 or 4 constant formula of the type derived from the Clapeyron-Clausius equation, which is not surprising, considering the complexity of the liquid and vapor involved. Recourse was then had to Biot's equation, with which a satisfactory fit was obtained. Columns 3, 4, and 5 give, respectively, the corresponding pressures calculated from this equation, and the absolute and percentage deviations of the observed values from those calculated.

Biot's equation: $\log p = a + b^{\alpha t} + c^{\beta t}$

$a = 6.109689$ $\qquad \log \alpha = \bar{1}.9992626992$

$\log b = 1.0229544$ (neg.) $\qquad \log \beta = \bar{1}.995996284$

$\log c = 1.9198970$ (neg.)

Between 270° and 550° the agreement is to within a few tenths of one percent. It seems probable that an even better fit could be obtained by using a special equation for this limited range only, but at best the gain would be small, and is outweighed by the advantages of a single equation for the whole range. Below 270° the mean deviation rises, and is over 2 percent from 210° to 270°; it is about 1 percent from 120° to 210°. The

curve, then, is simply the smoothed mean of a considerable number of observations. Below 120° the curve is an approximate exterpolation, since the error of measurement alone is quite high, and the occurrence of the melting point would mark a discontinuity.

Table II gives the vapor pressures for every ten degrees from 120° to 550°, as calculated from our equation.

B. *Results of Others.*

The results of other observers between these temperatures are listed in Table III, with corresponding pressures calculated from our equation, and deviations from the same. G indicates Gruener;[1] R and G, Ruff and Graf;[2] M, Matthies;[3] B, Bodenstein;[4] R, Regnault.[5]

TABLE III
Results of Others

Obs.	Temp. °C	p obs.	p calc.	diff.	percent
R and G	104.0	0.0115	0.0096	+ .0019	+19.8
G	104.4	0.0100	0.0103	− .0003	− 3.0
G	109.8	0.0134	0.0137	− .0003	− 2.2
R and G	110.8	0.0200	0.0159	+ .0041	+25.8
R and G	114.5	0.0285	0.0207	+ .0072	+34.7
G	120.5	0.0351	0.0314	+ .0037	+11.8
R and G	123.8	0.0535	0.0381	+ .0154	+40.0
R and G	131.9	0.081	0.0622	+ .0188	+30.3
R and G	132.2	0.079	0.0674	+ .0116	+17.2
R and G	133.1	0.088	0.0714	+ .0166	+23.2
R and G	141.0	0.131	0.115	+ .016	+13.9
R and G	147.0	0.192	0.162	+ .030	+18.5
R and G	157.0	0.332	0.284	+ .048	+16.9
R and G	162.0	0.403	0.359	+ .044	+12.2
R and G	172.0	0.629	0.608	+ .021	+ 3.5
R and G	189.5	1.38	1.36	+ .02	+ 1.5
R and G	211.3	3.14	3.32	− .18	− 5.5
M	241.8	8.45	9.75	− 1.30	−13.2
M	265.0	20.5	19.9	+ .6	+ 3.0
M	306.5	53.5	59.0	− 5.5	− 9.3
M	341.7	105.5	128.8	−23.3	−17.9
M	352.5	133.0	160.5	−30.5	−18.7
M	363.0	176.0	196.3	−20.3	−10.2
B	374	240	240.9	− .9	− 0.5

[1] J. Am. Chem. Soc., **29**, 1395 (1907).
[2] Z. anorg. Chem., **58**, 209 (1908).
[3] Physik. Z., **7**, 395 (1906).
[4] Z. physik. Chem., **20**, 113 (1899).
[5] Mém. de l'Acad., **26**, 339 (1862).

TABLE III (continued)

Obs.	Temp. °C	p obs.	p calc.	diff.	percent
M	379.4	250.1	265.7	− 15.6	− 5.9
R	390	272.3	320.2	− 47.9	−14.9
B	393	336	340.3	− 3.7	− 1.1
R	400	329.0	379.5	− 50.5	−13.2
R	410	395.2	447.2	− 52.0	−11.6
B	410	443	450.7	− 6.3	− 1.4
R	420	472.1	524.4	− 52.3	−10.0
B	427	580	584.7	− 4.7	− 0.8
R	430	561.0	612.1	− 51.1	− 8.2
R	440	663.1	710.7	− 47.6	− 6.7
B	444.53	760	759.5	+ .5	+ 0.1
R	450	779.9	822.1	− 42.2	− 5.1
R	460	912.7	946.5	− 32.8	− 3.5
R	470	1063	1086	− 23	− 2.0
R	480	1232	1241	− 8	− 0.7
R	490	1423	1414	+ 9	+ 0.6
R	500	1635	1605	+ 30	+ 1.9
R	510	1872	1815	+ 57	+ 3.1
R	520	2133	2048	+ 85	+ 4.1
R	530	2422	2303	+119	+ 5.2
R	540	2739	2583	+156	+ 6.0

(Regnault's results are given here only to four figures).

Gruener, and Ruff and Graf used the gas current saturation method, assuming sulfur vapor to be S_8. Preuner and Schupp[1] have since shown that the vapor density of sulfur is less than this, even at 100°. The correction, based on their data, would range from 3 percent at 105° to 6 percent at 210°. If this correction be made, it is seen that the highest observation of Ruff and Graf falls almost exactly on our curve, but that their other results are increasingly high as we come down the temperature scale. Gruener's two lower values also fall on our curve, when corrected, but his highest one is above it. This last is the most uncertain, according to Gruener, who states that his apparatus was not well adapted to higher temperatures. It may be noted that Gruener's results below 100° fall consistently lower than those of Ruff and Graf, and the latter explain this discrepancy by criticism of details of Gruener's technique. It is striking that Ruff and Graf agree with us at the higher pressures, where, as has been pointed out, systematic error would be most likely to make our results low.

Matthias employed the boiling point method, measuring pressures with a manometer or a McLeod gauge, and temperatures with a thermocouple. His results below 240° are omitted, since he considers that they are somewhat doubtful; they fall increasingly lower than our curve. With one exception

[1] Z. physik. Chem., **68**, 129 (1909).

his observations lie below our curve. It can be understood that at these low pressures, with a liquid of the viscosity of sulfur, the boiling point method presents considerable difficulty. He does not give details of the method of heating, nor of precautions to prevent superheating.

The results of Bodenstein show very good agreement with our curve; considering that he gives his temperatures only to the nearest degree, the agreement is practically within his experimental error.

In view of the advances in technique which have taken place since the time of Regnault, the comparison of his results serves to confirm the high opinion in which his work has always been held.

A futher comparison with previous measurements may be obtained near the boiling point. Mueller and Burgess (loc. cit.) have shown that for several degrees on either side of the boiling point the temperature may be computed from the equation:

$$t = t_{760} + 0.0910(p\text{-}760) - 0.000049(p\text{-}760)^2$$

If we assume $t_{760} = 444.57°$, and calculate points on either side of the normal boiling point, we obtain the following results for the two equations:

pressure	M and B	Ours	Dev. (°C)
793.86	447.590	447.570	−.020
706.46	439.543	439.570	+.027

This small deviation is in the same direction, and of the same order of magnitude, as the slight lack of fit already referred to; *i.e.* our calculated curve similarly crosses our observational curve at a very small angle, at the boiling point.

In conclusion, it appears that the most serious divergence from our curve, of observations made under favorable conditions, is that of the results of Ruff and Graf. Gruener, using the same method as they did, likewise obtained lower results, in consonance with our own findings.

C. *Accuracy of Our Results.*

The maximum absolute error in temperature measurement we estimate as 0.05°. Above 400° this is the principal source of uncertainty in the results; below 300° it is entirely negligible, compared to errors in pressure measurement. Pressures measured with isoteniscope and mercury gauge may be in error by not more than 0.3 mm above 300°, and rather more, below, due to difficulty in levelling. For lower pressures, measured with the McLeod gauge, the error is 0.1 − 0.2 mm, due almost entirely to uncertainty in levelling the isoteniscope. In the vaporization bulb method, apart from possible systematic error, the uncertainty is about 1 percent, except at the lowest pressures, where it is higher.

The following summary may be made:

Temp. range	Estimated mean error of observation (percent of pressure)
100°—120°	10 percent
120—210	1
210—260	2.5
260—300	1
300—350	0.3
350—475	0.1
475—550	0.2

III. Related Thermal Data

A. *Heat of Vaporization.*

Having obtained a reasonably good equation for the vapor pressure curve of sulfur, we may calculate the latent heat of vaporization from the Clapeyron-Clausius equation:

$$L = T(v_g - v_l)(dp/dt)$$

dp/dt is obtained by differentiating Biot's equation. v_g may be found from the vapor density data of Preuner and Schupp, (loc. cit.), while v_l is appreciable, relatively to v_g, only at the extreme upper end of the curve. The first two columns of Table IV give temperatures and corresponding heats of vaporization in cal/g. The same values are shown graphically by the solid curve in Fig. 2(A).

It is seen that L diminishes rapidly to a minimum at about 365°, and then rises. The general rule for normal substances is that L should diminish continuously, becoming zero at the critical temperature. Some substances, which are associated in the liquid phase, show a maximum at some temperature, (e.g. acetic acid[1]), but for a liquid to show a minimum heat of vaporization is unusual. The explanation appears to be given by the results of Preuner and Schupp (loc. cit.) They calculate the relative quantities of different molecules in the saturated vapor at different temperatures, and show that S_2 does not begin to appear till above 300°, and then only in small amount. However, they show from equilibrium considerations that $S_8 \longrightarrow 4S_2$ requires about 370 cal/g, while we see that $S_{liq} \longrightarrow S_{vap}$, at these temperatures, requires only 70—80 cal/g. If we calculate the amount of energy needed to form the percentage of S_2 given by Preuner and Schupp, and subtract it, at each temperature, from our heats of vaporization, we obtain the values in column 3 of Table IV, and the dotted curve in Fig. 2 (A). It appears that the abnormal rise is caused entirely by this dissociation in the vapor phase, and the fact that the "corrected" curve follows the normal course seems to confirm Preuner and Schupp's reasoning.

By interpolation for the normal boiling point we obtain the value of L = 69.5 cal/g. This may be compared with two recent determinations. Beck-

[1] Ramsay and Young: J. Chem. Soc., **49**, 790 (1886).

mann and Liesche[1] obtained the ebullioscopic constant and heat of vaporization of sulfur from vapor pressure data by Bodenstein, and found the value 64.8 cal/g. They assumed the molecular weight to be identical in liquid and vapor, namely 230.6. If we use 214, the value of Preuner and Schupp,

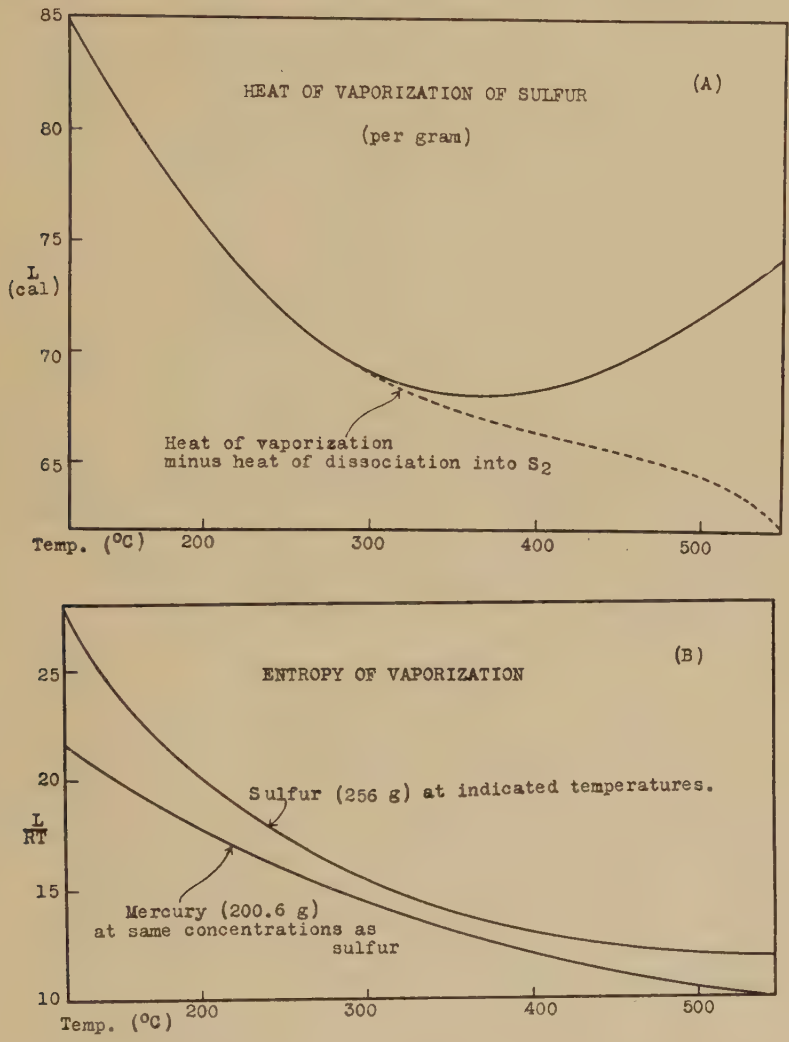

FIG. 2

we obtain, by their method, 71.3 cal/g. It will be shown later that the molecular weights of liquid and vapor are probably not very different at these temperatures. Awberry[2] determined the heat of vaporization of sulfur at the boiling point calorimetrically, and found 79 cal/g, with an estimated error of 2 percent.

[1] Z. anorg. Chem., **85**, 31 (1914).
[2] Proc. Phys. Soc. London, **39**, 417 (1927).

TABLE IV

Heat of Vaporization of sulfur

Temp. °C	L (cal/g)	L minus heat of dissociation to S_2 present in vapor	Temp. °C	L(cal/g)	L minus heat of dissociation to S_2 present in vapor
120	84.8		320	68.6	68.3
140	82.4		340	68.2	67.7
160	79.7		360	68.1	67.2
180	77.5		380	68.2	66.8
200	73.7		400	68.4	66.4
220	75.5		420	68.7	66.0
240	72.3		440	69.3	65.6
260	71.0		460	70.0	65.2
280	70.0		480	70.9	64.9
300	69.1		500	71.8	64.1
			520	72.9	63.6
			540	73.9	62.7

The accuracy of our figure depends on the values of dp/dt and the vapor density. We may obtain the former by differentiating the equation of Mueller and Burgess, (loc. cit) and find thereby L = 69.6, instead of 69.5 as computed from our equation. For the latter we have to depend on Preuner and Schupp, and there seems to be no reason for suspecting any error in their work at all approaching our lack of agreement with Awberry.

B. *Entropy of Vaporization.*

Hildebrand[1] has shown that, for normal liquids, molar entropies of vaporization are approximately equal at equal concentrations of saturated vapor. In particular, for a vapor concentration where log T − log p = 0.500, L/RT = 13.7 for normal liquids, while for associated liquids the value is decidedly higher. Sulfur attains this concentration at 364.5°, and at this temperature L/RT = 13.6, which would indicate that the molecular constitution of liquid and vapor are the same. If we compute the entropy of vaporization over the whole temperature range, a different conclusion is reached. Fig. II (B) shows graphically L/RT for 256g of sulfur, plotted against temperature, with a similar curve for mercury at corresponding concentrations. Mercury is chosen because accurate vapor pressure data are available;[2] Hildebrand has shown that, in common with other metals, it gives entropies of vaporization which are lower than those of "normal" liquids, such as hydrocarbons.

It is seen that the curve for sulfur rises at each end. At high temperatures, this is due to the formation of S_2 in the vapor, the liquid being relatively associated by contrast. At low temperatures the vapor is essentially S_8, and yet the high entropy of vaporization indicates marked association in the

[1] J. Am. Chem. Soc., **37**, 970 (1915).
[2] Menzies: Z. physik. Chem., **130**, 90 (1927).

liquid. This would call for a polymerized molecule, perhaps $(S_8)_2$, which dissociated rapidly with rise in temperature. Molecular weight determinations of sulfur in other solvents practically all give S_8, but partition experiments show that where different molecular forms are possible, a particular solvent usually dissolves only one type. Since the solvents used for sulfur have all been of one class, namely organic compounds, it appears that molecular weight data do not furnish a valid objection to the hypothesis stated above. Equally satisfactory would be the theory that there are different forms of S_8 molecules, possessing different quantities of energy. It is of interest to note that X-ray measurements of the lattice of rhombic sulfur[1] indicate that the crystal molecule may consist of 16 atoms.

Summary

1. Experimental determinations of the vapor pressure of sulfur have been made from 104° to 543°.

2. Constants have been calculated for an empirical equation which adequately represents these observations, and from it has been constructed a table of vapor pressures for each ten degrees, over this range. The results of other workers are compared with those given by this equation.

3. The heats of vaporization and entropies of vaporization have been calculated over this temperature range. Their abnormalities have been discussed in relation to the molecular constitution of liquid and vapor.

[1] Mark and Wigner: Z. physik. Chem., **111**, 398 (1924).